

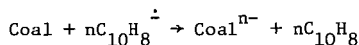
COAL ALKYLATION REACTION. THE CHARACTERISTICS  
OF THE ALKYLATION REACTIONS AND PRODUCTS

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INTRODUCTION

Sternberg and his associates found that the treatment of many coals with alkali metals in the presence of electron transfer agents formed polyanions which could be alkylated to form compounds which were soluble in common organic solvents including heptane and benzene (1). More recently, we discussed the proton and carbon nmr spectra of typical gpc fractions of polybutylated Illinois No. 6 coal (2). This work revealed that there were significant differences in these fractions with variations in the degree of aromaticity, the ratio of C-butylation to O-butylation, the extent of butylation on aliphatic and aromatic carbon atoms, and the amount of carbonyl and vinyl derivatives. In addition, the low molecular weight fractions contained paraffinic hydrocarbons which presumably were liberated as the coal matrix collapsed. The results obtained in this work are compatible with the essential features of the reaction process proposed by Sternberg and his associates (1,2). He suggested that the electron transfer agent, naphthalene, transfers electrons from the metal to molecular fragments in the coal. Under these conditions,



the aromatic molecules of the coal are reduced, and the basic anions produced under the experimental conditions react with acidic hydrogen atoms to yield aryloxides and stable carbanions. Ether cleavage and elimination reactions also occur under these experimental conditions. In addition, carbon-carbon bond cleavage reactions take place. Also, carbonyl compounds are reduced to semiquinones or ketyls. In the presence of sufficient concentrations of soluble electron transfer reagents, an equilibrium mixture of soluble and insoluble polyanions containing carbanions, aryloxides, mercaptides, ketyls, nitro-geneous bases and so forth is generated. Because few rearrangement reactions occur under basic conditions the structures of the anionic products are quite closely related to the structures of the molecular fragments in coal. These anionic compounds are readily alkylated by primary iodides. However, the alkylation reaction is complicated by competitive electron transfer reactions which yield butyl radicals. Thus, the coal alkylation reactions occur by the reactions of the nucleophilic anionic compounds with the alkyl iodide and by the reactions of the aromatic hydrocarbon compounds with the butyl radical.

The rich chemistry of the coal polyanion and the presumably close relationship between the structures of the coal polyanion and the initial coal molecules prompted us to study the reaction conditions and the reaction products carefully and then to examine the reaction of the coal polyanion with 90%-enriched butyl iodide-1-C-13.

#### EXPERIMENTAL PART

Materials.--Successful alkylations require the use of thoroughly purified reagents in an air and moisture-free environment. The reagents used in this work were all carefully purified by distillation or recrystallization shortly before use. The Illinois No. 6 coal samples (Anal.: C, 70.19; H, 5.18; N, 0.62; Cl, 0.14; S(pyritic), 0.82; S(sulfate), 0; S(organic), 2.71; O(by diff.) 11.43; Ash, 8.19) were dried at 100° in vacuo for 16 hrs. Tetrahydrofuran was refluxed in a nitrogen atmosphere over lithium aluminum hydride for 4 hrs prior to distillation from the hydride. The distillate was stored under argon. Tetrahydrofuran could not be purified as readily by distillation from potassium. We found that the resonances of vinyl, carboxyl and other unidentified groups were present in the nmr spectra of concentrated samples of the distillate when potassium was used as the purification reagent.

Preliminary Experiments.--Initial work centered on the study of the reaction of potassium with tetrahydrofuran and with naphthalene in tetrahydrofuran.

Potassium (20 mmol) was added to tetrahydrofuran (50 ml) under argon. Aliquots free of potassium were withdrawn periodically. These aliquots were hydrolyzed and titrated to determine the extent of the reduction of the solvent. This reaction was negligible even after 5 days, Figure 1A.

In the next experiment, potassium (20.1 mmol) was added to a stirred solution of naphthalene (3.10 mmol) in tetrahydrofuran (50 ml) under argon. The characteristic dark green solution of naphthalene radical anion and dianion formed within 4 min. Aliquots free of potassium were withdrawn from the reaction mixture. These aliquots were hydrolyzed and titrated to determine the extent of conversion of naphthalene to the radical anion and dianion. After about 4.5 hrs, the titrimetric procedure revealed that the naphthalene was converted to a mixture equal in reducing power to 80% dianions. The reaction was followed for 5 days. The results are shown in Figure 1B.

In the third experiment of this series, potassium (20.1 mmol) and naphthalene (3.10 mmol) in tetrahydrofuran (50 ml) were allowed to react for 4.5 hrs. Coal (0.860g) was then added. The reaction mixture immediately became brown. During the next several days the reaction mixture changed color as the reactions proceeded. Aliquots free of potassium but containing solid coal particles were withdrawn from this mixture and titrated to determine the extent of conversion of the coal to the coal polyanion. In certain instances, aliquots free of potassium and solid coal particles were withdrawn from the reaction mixture and titrated to determine the extent of conversion of the solid coal to soluble anionic substances. The reaction was allowed to proceed for 5 days at ambient temperature under argon. An aliquot of the mixture was then withdrawn to establish the extent of the reaction. The results are shown in Figure 1C.

The results obtained in several experiments revealed that  $21 \pm 1$  negative charges per 100 carbon atoms were introduced into the coal.

Coal Alkylation with Butyl Iodide-1-C-13.--Potassium (26.1 mmol) was added to a stirred solution of naphthalene (3.14 mmole) in tetrahydrofuran (45 ml) under argon. After 45 min, -325 mesh coal (1.00g) and an additional wash quantity of tetrahydrofuran (10 ml) were added. The mixture was stirred for 5 days. The excess potassium (2.98 mmol) was removed. A small quantity of insoluble coal (0.041g) was unavoidably lost in the removal of the metal. A solution of 90%-enriched butyl iodide-1-C-13 (6.88g) in tetrahydrofuran (10 ml) was added to the stirred solution in 15 min. This quantity corresponds to a 2-fold excess of the amount of reagent needed for the alkylation of a coal polyanion with 21 negative charges per 100 carbon atoms and naphthalene dianion. Potassium iodide began to precipitate from the reaction mixture almost immediately. The alkylation reaction was allowed to proceed for 2 days. Potassium iodide rapidly settled from the reaction mixture when stirring was interrupted.

The reaction mixture was then exposed to the atmosphere and the coal product was isolated. The mixture was centrifuged and the very dark brown, tetrahydrofuran-soluble material was removed by pipet. Fresh solvent was added to the residue and the mixture was stirred. The mixture was then centrifuged and the soluble material was removed by pipet. This procedure was repeated several times. The final extracts were clear, pale yellow solutions. The combined extracts were filtered through a  $1.4\mu$  frit. The filtrate was concentrated in vacuo at  $50^\circ\text{C}$  to yield a freely flowing, dark brown material (2.252g). Residual volatile materials were removed in several stages in vacuo. The amounts of material present after 2 hrs were 1.956g; after 16 hrs, 1.678g; after 41 hrs, 1.581g; and after 68 hrs, 1.521g. This product is dark brown and does not flow.

Water was added to dissolve the potassium iodide present in the tetrahydrofuran-insoluble material. The mixture was then stirred and subsequently centrifuged to yield a clear, yellow supernatant solution and a small residue. This residue was treated in the same way several times to extract all the water soluble materials. The final extracts were colorless and did not yield a precipitate when treated with sodium tetraphenylborate. The residue obtained in this way was dried in a stream of dry nitrogen to constant weight (0.686g).

The water-soluble material was filtered through a  $1.4\mu$  frit. An aliquot of the solution was treated with excess sodium tetraphenylborate. The potassium tetraphenylborate which precipitated was collected and dried. This analysis indicates that 18.1 meq of potassium ion were formed in the reaction.

The tetrahydrofuran-soluble portion of the butylated, carbon-13 labelled Illinois No. 6 coal (1.5208g) was chromatographed on silica gel (Baker, 60-200 mesh, 24g) to remove materials such as the electron transfer agent and the related reduction and alkylation products. These materials were eluted with pure hexane (about 250 ml) and 5:95 tetrahydrofuran: hexane (about 250 ml). The dried eluent weighed 0.9967g. The coal products were then eluted with pure tetrahydrofuran (about 250 ml) followed by 50:50 tetrahydrofuran: methanol (about 250 ml) and pure methanol (about 250 ml). The dried eluent weighed 0.5350g. The recovery was virtually quantitative.

A portion of the coal product (168.1 mg) was dissolved in pure tetrahydrofuran (2 ml) and chromatographed on Styragel(R) gpc columns (Waters Associates). Columns with a molecular weight exclusion limit of 10,000 (2 x 61 cm.) and 2,000

(2 x 61 cm.) were connected in series. Tetrahydrofuran was used as the mobile phase ( $0.36 \pm 0.01$  ml min<sup>-1</sup>). About 30 fractions (3.7 to 3.8 ml) were collected in each experiment. The tetrahydrofuran was removed in vacuo and a stream of filtered, dry nitrogen was used to remove the final traces of the solvent. The coal product obtained with C-13 labelled butyl iodide was partitioned into 17 fractions (total weight 178.4 mg). Samples to be used for nmr spectroscopy were dried thoroughly at 25° at about 5 torr for 40-45 hrs to remove the remaining traces of tetrahydrofuran.

The spectroscopic methods used in this study have been described previously (2).

Other Alkylation Experiments.--In other experiments, lithium and sodium were used in place of potassium. 1,2-Dimethoxyethane was used in place of tetrahydrofuran. Butyl chloride, butyl bromide, butyl mesylate, butyl triflate, and methyl iodide were used in place of butyl iodide. The conditions used in these experiments were very similar to the conditions used in the procedures described in the previous paragraphs. The isolation procedure was modified in those cases where the ionic salt, e.g. sodium iodide, was soluble in tetrahydrofuran. In these instances, the tetrahydrofuran-soluble product was washed with water to remove the salt prior to further study.

Repetitive Alkylation Reaction.--The tetrahydrofuran-insoluble materials were, in certain instances, subjected to a second alkylation reaction. In these cases, there were three notable differences in the experimental results. First, the green color of the naphthalene dianion persisted for a significantly longer time following the addition of the coal residue. Second, gas evolution, presumably butene-1, was detectable during the addition of butyl iodide or butyl mesylate but, significantly, not during the addition of methyl iodide. Third, the rate of formation of potassium iodide was much more rapid such that the rate difference between butyl iodide and methyl iodide was not evident.

The reaction products were separated into tetrahydrofuran-soluble and tetrahydrofuran-insoluble fractions as already described. The chromatographic separations and spectroscopic investigations were also performed as described.

## RESULTS AND DISCUSSION

The rates of reduction of tetrahydrofuran (A), naphthalene (B), and Illinois No. 6 coal (C) are shown in Figure 1. These preliminary experiments established that potassium reacted only very slowly with tetrahydrofuran under the experimental conditions used for the formation of the coal polyanion. Naphthalene was rapidly converted to a mixture of anion radicals and dianions under the same conditions. The initial reaction between the electron transfer reagent and the Illinois No. 6 coal was quite rapid. However, the reaction slowed to nearly constant rate after about 12 hours. During the last four days of reaction the coal molecules acquired about 0.1 negative charges per 100 carbon atoms per hour.

The titrimetric data indicated that the coal polyanions derived from this coal quite reproducibly had  $21 \pm 1$  negative charges per 100 carbon atoms when potassium was used as the reducing agent. The evidence obtained in the magnetic resonance work on the reaction products suggests that these negative charges reside largely on the oxygen atoms of the phenoxide and alkoxide residues and on the carbon skeletons of the aromatic fragments of the coal structure.

Potassium is a much more effective reducing agent than either sodium or lithium. This feature of the reaction is illustrated by the extent of reduction (measured by the number of negative charges per 100 carbon atoms) and the extent of alkylation (measured by the number of alkyl groups introduced and the weight of the reaction products). The results are summarized in Table I.

TABLE I  
THE REDUCTION AND ALKYLATION OF ILLINOIS NO. 6 COAL WITH  
LITHIUM, SODIUM, AND POTASSIUM

Reagent Pair	Reduction <sup>a</sup>	Alkylation <sup>b</sup>
Lithium, Butyl iodide	12.0	12.2 (0.78g)
Sodium, Butyl iodide	12.9	13.2 (1.17g)
Potassium, Butyl iodide	19.3	20.1 (1.52g)

<sup>a</sup>Negative charges acquired per 100 carbon atoms.

<sup>b</sup>Butyl groups introduced per 100 carbon atoms. The weight of tetrahydrofuran-soluble product obtained from 1.00g of coal.

The reactions of the coal polyanion with methyl iodide and butyl iodide were compared in tetrahydrofuran. The reaction could be monitored quite readily by the rate at which potassium iodide precipitated from solution. We estimate that methyl iodide is about 10-fold more reactive than butyl iodide under these conditions. This result, of course, suggests that the SN<sub>2</sub> reactions of the coal polyanion are more significant than the electron transfer reactions. Although there is a clear distinction in the reaction rate, the extent of the alkylation reaction is the same for methylation and butylation with about 21 alkyl groups introduced per 100 carbon atoms. The amount of tetrahydrofuran-soluble alkylation product is also similar for methylation and butylation under comparable conditions.

The observations concerning the butyl halides and sulfonates are summarized in Table II.

TABLE II  
ALKYLATION REACTIONS WITH BUTYL DERIVATIVES

Reagent, equivalents <sup>a</sup>	First Reaction		Second Reaction		Total %
	Solubility, <sup>b</sup> %	Residue, <sup>c</sup> g	Solubility, <sup>b</sup> %	Residue, <sup>c</sup> g	
BuCl, 2.0	23	1.00	--	--	--
BuBr, 2.0	51	0.64	--	--	--
BuI, 2.0	62	0.49	74	0.18	79
BuOSO <sub>2</sub> CH <sub>3</sub> , 2.0	64	0.51	polymer	--	--
BuOSO <sub>2</sub> CF <sub>3</sub> , 2.0	polymer	--		--	--

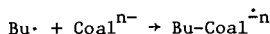
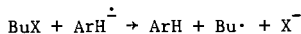
<sup>a</sup>Based on the number of negative charges acquired by the coal.

<sup>b</sup>The percentage of the original coal which has been converted to soluble product. The values reported here have been corrected for the extent of the alkylation reaction.

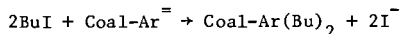
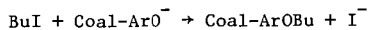
<sup>c</sup>The weight of the tetrahydrofuran-insoluble residue. No correction has been applied for either alkylation or mineral matter.

The reactions of the potassium coal polyanion with the butylation reagents differed markedly. Both the percentage of soluble product and the weight of residue indicate that the reactions of the chloride and the bromide are distinctly less effective than the reactions of the iodide. The butyl sulfonate esters were much more reactive. In one case, the mere addition of freshly distilled butyl triflate to tetrahydrofuran at room temperature caused the polymerization of the solvent. In the other case, the addition of butyl mesylate to the reaction mixture was effective for the production of soluble products in 64% conversion. However, when the reaction was repeated with the residue, a polymerization reaction ensued and a gas, 1-butene, was evolved from the reaction mixture.

These observations indicate that butyl iodide is adequately reactive for the alkylation of the polyanion. This reagent effectively converts more than 90% of the original carbonaceous matter in the coal to soluble alkylation products. The fact that the reactions of butyl chloride and butyl bromide do not give similar results suggests very strongly that SN2 reactions rather than electron transfer reactions are primarily responsible for the production of soluble materials. This interpretation is based on the fact that the reactivities of nucleophiles with butyl iodide, bromide, and chloride are in the approximate order 100:60:1 and that these substitution reactions are all slow relative to the electron transfer reactions of the butyl halides with anion radicals. To illustrate, the rate constants for the reactions of primary alkyl iodides with anion radicals of the kind formed under the conditions of these experiments are about  $10^7$  l/mole sec (3). The rate constants for the reactions of primary alkyl iodides with nucleophiles are much smaller, only about 10 l/mole sec in the fastest processes (4). Thus, we infer that the butyl halides all undergo rapid electron transfer reactions to produce butyl radicals during the initial stages of the alkylation process. We also infer that this process is less important



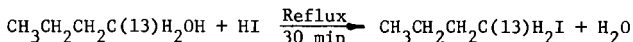
for the formation of soluble products than the alkylation reactions



which proceed much more slowly. Indeed, we observed that the precipitation of potassium iodide from the reaction of butyl iodide with the coal polyanion appeared to be complete only after about 24 hrs. Thus, the much slower reactions of the polyanion with the other halides would not be complete in 48 hrs.

In another experiment, we tested the utility of 1,2-dimethoxyethane as a solvent for the reaction. The results obtained in this experiment revealed that the coal polyanion was formed to the same extent as in tetrahydrofuran. In addition, the alkylation of the polyanion with butyl mesylate proceeded to give 65% soluble product. This datum is comparable with the result for butylation in tetrahydrofuran, 64%. Hence both solvents are equally useful for the alkylation reaction.

When we were satisfied that the alkylation reaction could be accomplished both effectively and reproducibly, we undertook the synthesis of C-13-enriched butyl iodide. Conventional procedures were used to produce the desired compound in 90% isolated yield using concentrated hydroiodic acid.



The coal alkylation reaction was carried out using the enriched compound and the products were separated using the procedures described in the Experimental Part. The proton and carbon nmr spectra of one fraction (comparable to fraction 9 in the previous report (2)) are presented in Figures 2 and 3.

The proton nmr spectra of the coal products obtained in this work are quite similar to the spectra of the products obtained by Sun and Burk and discussed previously (2). No additional comments on this aspect of the work are necessary.

The carbon nmr spectra, on the other hand, provide much new information concerning the alkylation reaction. To illustrate, the resonances at  $\delta 67.7$ ,  $72.9$ , and  $64.2$  indicate that O-butylation has occurred dominantly on aryloxides with concomitant butylation on alkoxide and possibly carboxylate fragments. The broad band of resonances at  $\delta 35$  indicate that C-butylation is also important and that butyl groups are bonded to quaternary and tertiary  $\text{sp}^3$  carbon atoms and possibly to aromatic carbon atoms. These results and the other spectroscopic data for other fractions enriched in carbon-13 will be discussed.

#### ACKNOWLEDGEMENT

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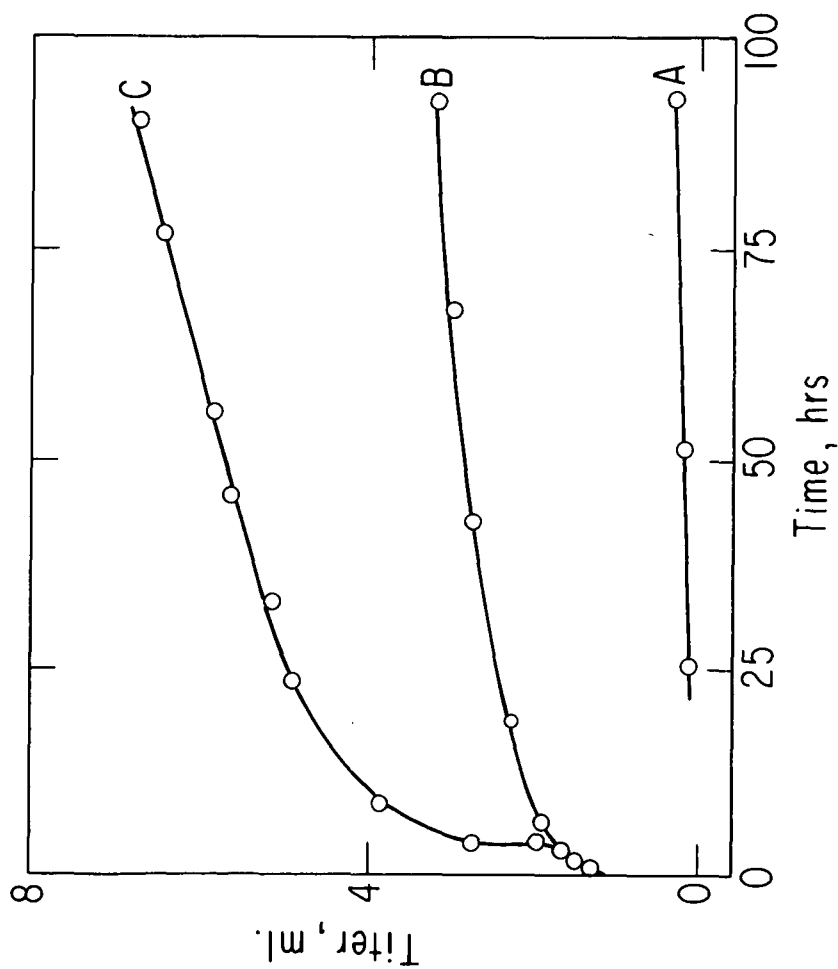


Figure 1.—The rates of reduction of tetrahydrofuran (A), naphthalene (B), and Illinois No. 6 coal (C) are presented by a comparison of the titer required for aliquots of separate reaction mixtures over 100 hrs.



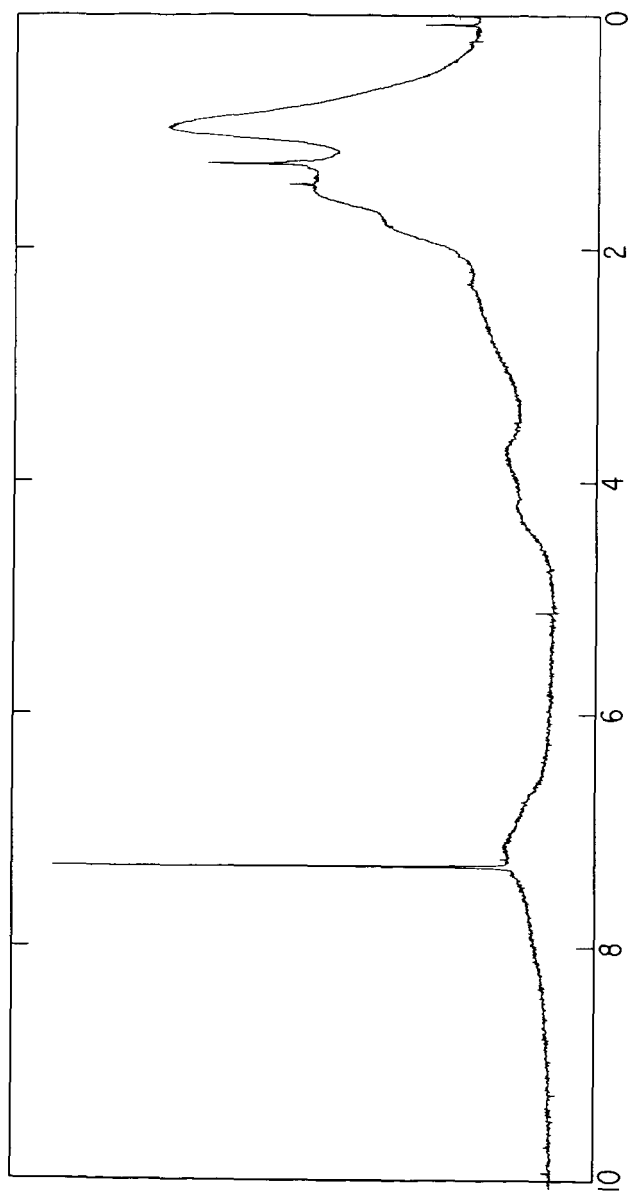


Figure 2.--The proton nmr spectrum of a representative fraction of coal butylated with the C-13 enriched reagent. The intense signal at  $\delta 7.3$  results from residual chloroform.

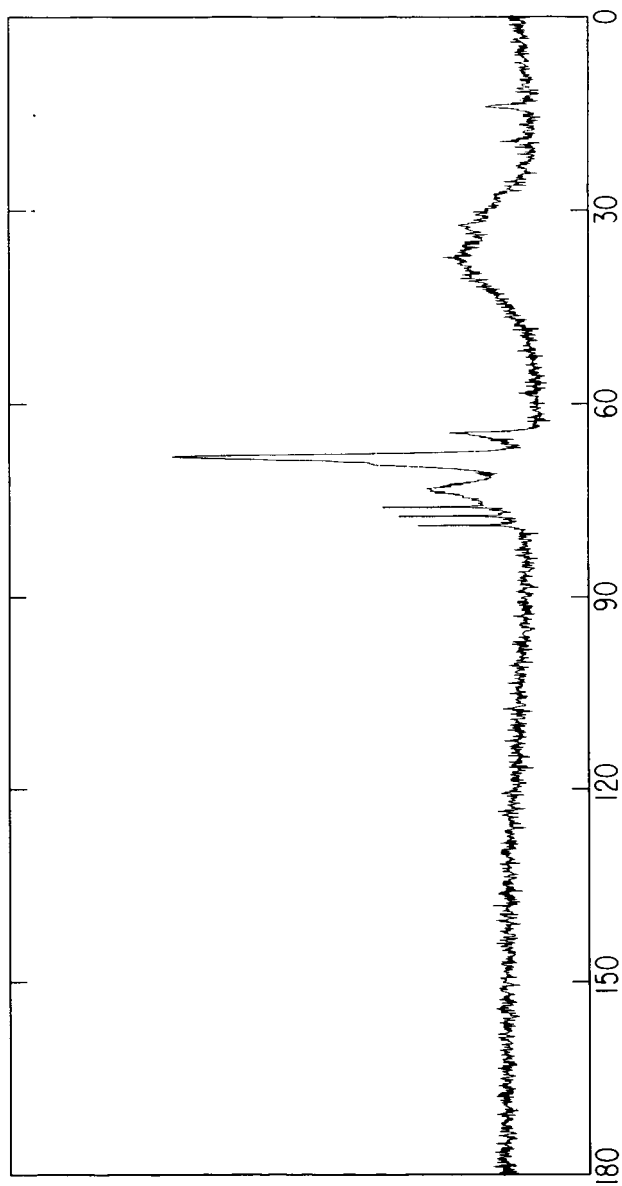


Figure 3.--The carbon nmr spectrum of a representative fraction of coal butylated with the C-13 enriched reagent. The three sharp signals at about  $\delta 77$  result from chloroform.